Structural Transitions and Magnetic Structure in NH_4CuCl_3 via ^{14}N-NMR

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We report results of ^{14}N-NMR experiments on NH_4CuCl_3 at the magnetic field of 7 T, where the 1/4-magnetization plateau is observed at low temperatures. The quadrupole splitting parameter ν_z splits below 70 K, indicating a structural phase transition. At 4.2 K, eight N sites with distinct values of both ν_z and the magnetic hyperfine shift K_z are resolved in the NMR spectrum for general field directions. We then conlude that the magnetic structure in the 1/4-plateau does not break the symmetry of the crystal. Based on the NMR and the recent neutron scattering results by Rüegg *et al.* [Phys. Rev. Lett. 93 (2004) 037207], we propose that triplet dimers in the 1/4-plateau is formed not between the nearest neighbor pairs but over different chains.

Magnetization plateaus in quantum spin systems have attracted strong recent interest as a novel example of quantum many body effects. Oshikawa formulated a necessary condition for magnetization plateaus in arbitrary dimensions,[1)] which in certain cases predicts that the periodicity of the ground state wave function is larger than the periodicity of the crystal. Such a magnetic superlattice should be a consequence of localization of magnetic excitations due to repulsive interactions and bear common physics to a number of interesting quantum many body phenomena such as Mott transition and charge ordering. Spontaneous symmetry breaking was indeed observed in the 1/8 magnetization plateau phase of the frustrated 2D dimer system $SrCu_2(BO_3)_2$.[2)] NH_4CuCl_3 has been considered as another candidate since magnetization plateaus were observed at 1/4 and 3/4 of the saturated magnetization but not at 1/2.[3)]

The crystal structure of NH_4CuCl_3 has the space group $P2_1/c$ at room temperature, in which Cu^{2+} ions form zigzag chains along the a-axis (Fig. 1).[4)] This is identical to the structure of $TlCuCl_3$ and $KCuCl_3$, which have dimer singlet ground states at zero magnetic field with a finite energy gap to the triplet excitations. The gap can be reduced by the field and an antiferromagnetic order appears above a critical field at which the gap vanishes. This phenomenon is best described as the Bose condensation of triplets .[5)] In contrast, NH_4CuCl_3 shows an antiferromagnetic order at zero-field[6),7)] and the magnetization increases continuously from zero field.[3)] Since all Cu sites are equivalent in the $P2_1/c$ structure, the 1/4 and the 3/4 plateaus in NH_4CuCl_3 must be accompanied by magnetic superstructure breaking the crystal symmetry if the crystal structure remains unchanged down to low temperatures.

In contradiction to this expectation, various experiments indicate existence of inequivalent Cu sites with different magnetic characters. Specific heat shows a Schottkey-type peak at zero-field indicating that the majority of spins are in singlet

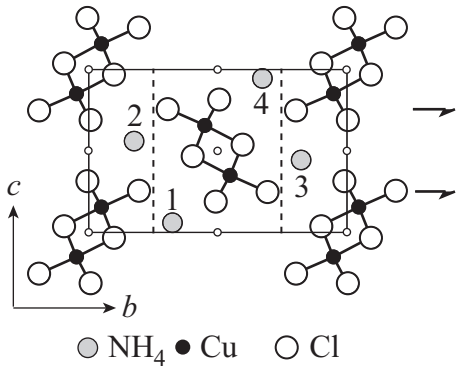

Fig. 1. Crystal structure of NH_4CuCl_3 at room temperature (space group $P2_1/c$) viewed along the a-axis. The inversion center, the b-screw axis, and the c-glide plane, are shown by the circles, the arrows, and the dashed lines, respectively.

states, in addition to an anomaly at T_N=1.3 K due to antiferromagnetic ordering of the rest of spins.[6] Existence of singlet dimers in the ground state was confirmed by the observation of two dispersive finite energy excitations at 1.6 meV and 3 meV by ESR[8] and neutron scattering[9] experiments. Both modes are only weakly dispersive.[9] NMR experiments on a single crystal enriched with ^{15}N isotope (spin 1/2) revealed splitting of the spectrum below 70 K for the external fields of 3 T and 6 T.[10] This splitting cannot be due to formation of magnetic superstructure because the magnetization plateau does not appear at 3 T. Since the magnetic susceptibility shows no anomaly around 70 K, the splitting of ^{15}N-NMR lines is likely to be due to lowering of crystal symmetry caused by ordering of NH_4 molecules as detected by the infrared absorption measurements.[11] The structural transition at 70 K was also suggested by elastic anomalies.[12] Based on these experimental results, Matsumoto proposed a model consisting of three distinct dimer sublattices with different energy gaps generated by structural distortion.[13] In this model, the plateaus correspond to successive saturation of each sublattice dimers. The recent neutron diffraction experiments[7] revealed that the structural transitions occur in two steps. First, the intensity of (001) reflection begins to increases below 156 K, indicating breaking of the c-glide symmetry. Then the reflection at (hkl) with half integer k appears below 70 K, pointing to doubling of the unit cell along the b-axis.

In this paper, we report results of NMR experiments on ^{14}N nuclei (spin 1) in a twin free single crystal of NH_4CuCl_3 at 7 T where the 1/4 plateau appears at low temperatures. The NMR spectra were obtained from the Fourier transform of the spin-echo signal. The ^{14}N-NMR spectra generally consist of two resonance lines at the following frequencies split by the electric quadrupole interaction,[14]

$$f_{\pm} = (1 + K_z)\gamma_n H_0 \pm \nu_z,\ \nu_z = (3eQ/4h)V_{zz}. \tag{1}$$

Here, γ_n is the nuclear gyromagnetic ratio, Q is the nuclear quadrupole moment, H_0 is the external field, K is the magnetic hyperfine shift, and $V_{zz} = \partial^2 V/\partial z^2$ is the zz-component of the electric field gradient tensor, where z is the field direction. The values of K_z and ν_z were determined as a function of temperature and field direction.

While the electric field gradient reflects the local symmetry of the crystal structure, the magnetic hyperfine shift is determined by the spin density distribution. ^{14}N-NMR thus allows us to examine correlation between structural and magnetic properties, in contrast to ^{15}N-NMR, from which one can obtain only the magnetic hyperfine shift.

The four N atoms in a unit cell are equivalent at room temperature because they transform each other by the symmetry operations of $P2_1/c$ group (Fig. 1). A pair of N sites should yield identical NMR spectrum if the field direction is invariant under the symmetry operation which transforms one N site to the other. This is always satisfied for the pair of sites related by inversion (1 and 4, or 2 and 3 in Fig. 1), while those pairs related by the *b*-screw (1 and 3, or 2 and 4) or the *c*-glide (1 and 2, or 3 and 4) give the same values of K_z and ν_z when the field is parallel to the *b*-axis or in the *ac*-plane. The observed NMR spectra are compatible with these conditions above 160 K. This enabled precise alignment of the *b*-axis along the field.

With the field set along the *b*-axis and with decreasing temperature, we found that ν_b begins to split below 160 K (Fig. 2 (a)). The splitting is very small, about 0.8 kHz at 80 K compared to ν_b=29 kHz. Moreover, the spectra show at most two set of quadrupole split lines for any field directions. These results led us to conclude that the *b*-screw and the *c*-glide symmetries are marginally broken below 160 K but the inversion symmetry is preserved. Therefore, the space group should be $P\bar{1}$. This is consistent with the observation of (001) reflection by neutron diffraction.[7)]

With further decreasing temperature, the NMR spectrum develops a drastic change. We show in Fig. 2 (b) the temperature variation of the NMR spectrum for the field approximately parallel (within 2°) to the $c*$-axis. The spectrum at 80 K shows only one set of lines, since the splitting of ν_z is accidentally nearly zero and the splitting of K_z is also smaller than the experimental resolution. The lines begin to split at T_c=69 K, clearly indicating a phase transition. At 4.2 K, the NMR spectrum consists of eight lines. The spin-echo signal for these lines oscillates as a function

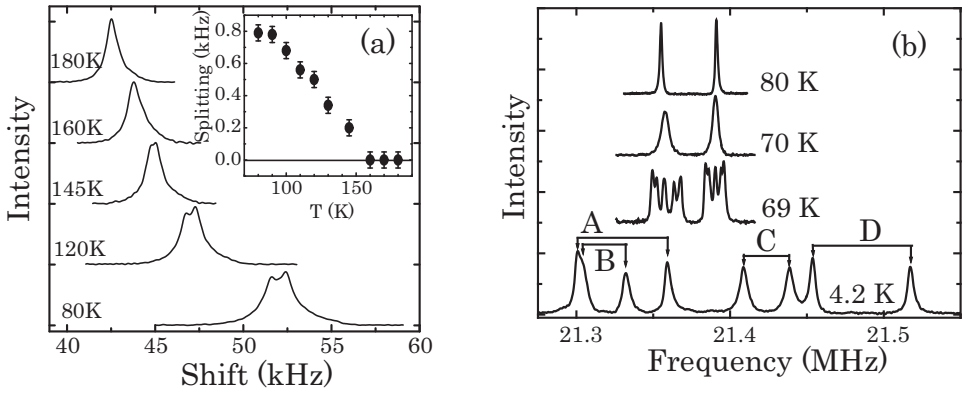

Fig. 2. (a) Temperature variation of the NMR spectrum in the magnetic field of 7 T along the *b*-axis. Although one peak of the quadreupole split pair of lines is shown here, the other peak also shows similar splitting below 160 K. The interval of the split peaks is plotted against temperature in the inset. (b) Temperature variation of the NMR spectrum below 80 K in the magnetic field of 7 T approximately parallel to the c^*-axis.

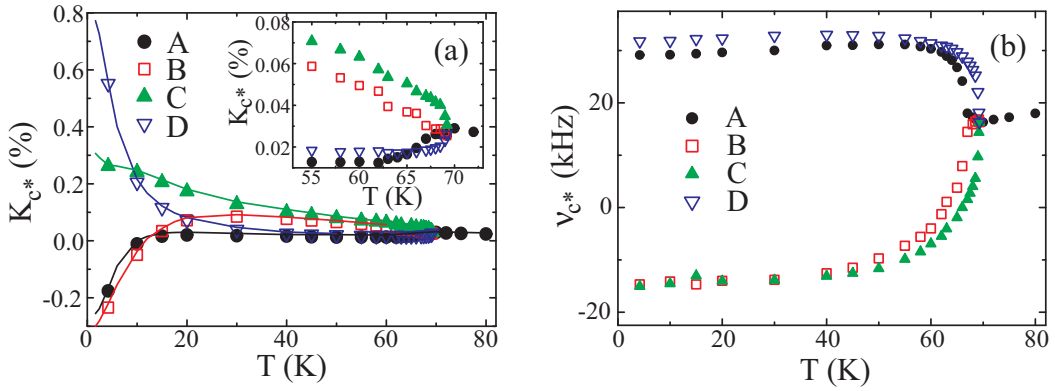

Fig. 3. Temperature dependence of (a) K_{c*} and (b) ν_{c*} for the sites A∼D shown in Fig. 2 in the field of 7 T approximately parallel to the c^*-axis.

of the separation time τ between the $\pi/2$- and the π-pulses. It is known that the quadrupole interaction causes such oscillation and its frequency is equal to $2\nu_z$.[15] This allowed us to classify the eight lines into four pairs of quadrupole split lines (A∼D in Fig. 2) originating from the same sites. The values of K_{c*} and ν_{c*} for each site were then determined from Eq. (1) at various temperatures as shown in Fig. 3.

The temperature dependences of K_{c*} and ν_{c*} are strikingly different, although both quantities begin to split at T_c. K_{c*} shows only minor variation near T_c but changes substantially at low temperatures. Similar temperature dependence was observed for K_b by Shimaoka *et al.*[10] In contrast, ν_{c*} changes rapidly in a temperature range close to T_c but becomes almost T-independent at low temperatures. These results indicate a second order structural phase transition at T_c, consistent with earlier experiments, and irrelevance of magnetic interactions in driving the transition. The structural change, most likely associated with long range orientation order of NH_4,

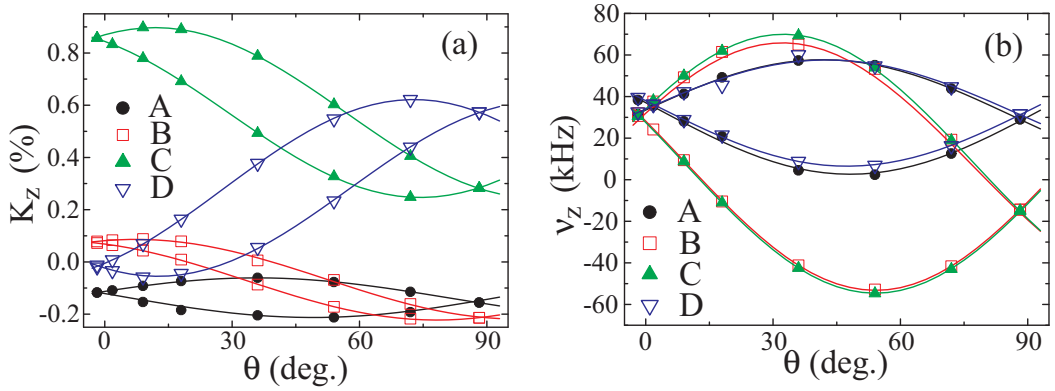

Fig. 4. Angular dependence of (a) K_z and (b) ν_z for sites A∼D in the magnetic field of 7 T rotated in $b - c^*$ plane. θ is an angle between the magnetic field and the b axis. The lines show the fitting described in the text.

would significantly modify the exchange interactions and lead to distinct magnetic characters for different sites at low temperatures. We should note, however, that an isolated NH_4 molecule with tetrahedral symmetry does not contribute to the electric field gradient at the N nuclei. Close examination of the data in Fig. 3(b) reveals a peculiar feature. While ν_Q at the sites C and D changes rapidly immediately below T_c, onset of the rapid change in ν_Q at the site A and B is shifted to a lower temperature by about 2 K. We do not have any explanation yet for such behavior.

The angular dependences of K_z and ν_z at 4.2 K were measured with the magnetic field rotated approximately from the b-axis ($\theta = 0°$) to the c^*-axis ($\theta = 90°$) as shown in Fig. 4. Within the experimental resolution, four distinct values of K_z and ν_z are obtained for $\theta \sim 0°$ and $\theta \sim 90°$. Each of these values splits into two for other field directions. The angular dependence of K_z and ν_z can be fit well to the form $\alpha + \beta\cos(2\theta + \gamma)$, where α, β, and γ are constants, as shown by the lines in Fig. 4. We found that the θ-dependences of both K_z and ν_z for the two branches of each pair (A$\sim$D) are approximately symmetric with respect to $\theta \sim 0°$ and $\theta \sim 90°$, indicating that the two branches are approximately related by the c-glide operation. Therefore, breaking of the c-glide symmetry must be still marginal in the low temperature phase. The data of K_z and ν_z both show that there are at least eight N atoms in a unit cell. An important consequence is that the magnetic structure (spin density distribution) does not necessarily break the crystal symmetry. This is consistent with the various experimental evidences mentioned earlier that the 1/4-plateau state emerges at low temperatures without symmetry breaking.

Now we discuss the magnetic structure of the 1/4-plateau based on the present NMR results and the neutron results by Rüegg *et al.*[7] According to the neutron data, unit cell doubling occurs along the b-direction but not along other directions. Then the unit cell of the low temperature phase contains eight N atoms. If these sites were paired by inversion symmetry, only four sites should be distinguished by NMR for any field direction. From our observation of eight distinct values of ν_Q and K_z for general field directions, we conclude that the inversion symmetry must be broken in the low temperature phase, i.e. the space group should be P1. Although Rüegg *et al.* concluded $P\bar{1}$ symmetry,[7] their argument was based on the earlier ^{15}N-NMR data,[10] which reported spectra only along the b-axis.

We assume that in the 1/4-plateau state, 1/4 of the Cu spins form nearly fully polarized triplet while the rest of spins are in singlet states, as suggested by various experiments mentioned earlier. The question then is where the fully polarized spins are located. All previous studies[7),13] assumed that triplets are formed over 1/4 of the nearest neighbor dimers as shown in Fig. 5(a). This spin configuration, however, preserves inversion symmetry but completely destroys the c-glide symmetry. Since the magnetic hyperfine field at the N sites should be determined primarily by the arrangement of fully polarized spins, this model is clearly incompatible with the approximate c-glide symmetry evidenced by the angular dependence of K_z. This configuration also yields similar values of K_z for those pairs related by inversion, leading to only four distinct values of K_z. This is again inconsistent with the observation of eight distinct values of K_z for general field directions.

This lead us to propose that the triplet dimers must be formed over different

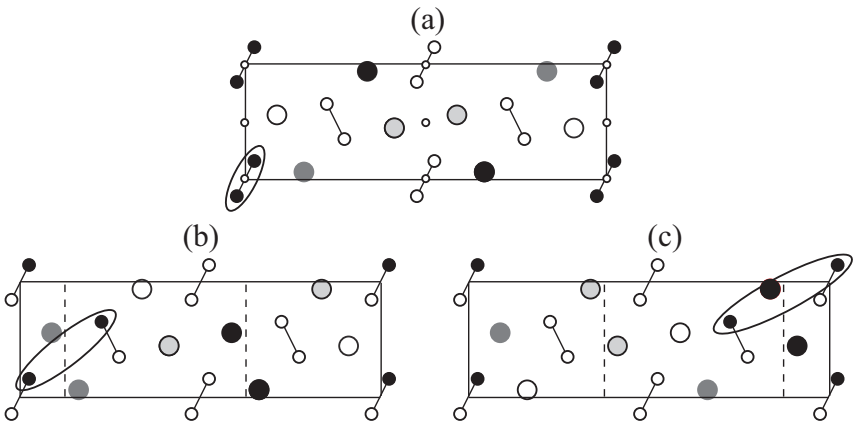

Fig. 5. Possible magnetic structure of the 1/4 plateau state. The small filled (open) circles show the triplet (singlet) Cu sites. Large circles show the N atoms. The dashed lines in (b) and (c) indicate the approximate *c*-glide plane preserved in each spin configuration.

chains as shown in Fig. 5 (b) or (c). The spin configuration in Fig. 5 (b) (Fig. 5(c)) has the *c*-glide plane at y=1/8 and 5/8 (y=3/8 and 7/8). Therefore, the angular dependence of K_z should also satisfy the approximate glide symmetry, consistent with our observation. Also the inversion symmetry is completely destroyed in these configurations, accounting for eight distinct values of K_z for general field directions. Although the four different symbols for NH_4 molecules in Fig. 5 (b) and (c) should correspond to the sites A∼D identified by our NMR data (Figs. 3 and 4), unambiguous assignment has not been made yet. At first sight, triplet dimers over such a long distance might appear very unlikely, since the strongest exchange interaction in $TlCuCl_3$ and $KCuCl_3$ is located between nearest neighbor pairs, stabilizing the dimer singlet state.[16)–18)] However, we note that NH_4CuCl_3 and other two compounds may have completely different exchange coupling scheme, because there is no similarity at all in the magnon dispersion observed by neutron scattering experiments. Moreover, since NH_4 molecules are located near the exchange path stabilizing the triplet dimers in Fig. 5 (b) and (c), orientation of NH_4 molecules should significantly modify the exchange coupling, accounting for the extremely strong spin-lattice coupling in this compound.

In conclusion, our ^{14}N-NMR experiments revealed that the structural transition at 69 K produces sufficiently large number of inequivalent Cu sites at low temperatures so that 1/4-magnetization plateau can emerge without symmetry breaking. The angular dependences of the magnetic hyperfine shift and the quadrupole splitting parameters combined with the published neutron results strongly suggest that the fully polarized triplets in the 1/4-plateau are formed not between the nearest neighbor pairs but over distant Cu spins on different chains.

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